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REACTOR GAS DRIER CONDENSATE WASTE -- DECONTAMINATION STUDIES

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L. F. Coleman

INTRODUCTION

Reactor coolant gases used in the production reactors are circulated through silica gel drier beds to remove accumulated water. The water and adsorbed or dissolved gases collected on the silica gel are removed when necessary by heating. The volume of condensate from silica gel bed regeneration is normally measured and the condensate routed to the river or to dry wells. As a result of neutron irradiation of the coolant gas C^{14} containing species are found in the drier condensate.

Concern was expressed regarding the amount of C^{14} in the condensate, particularly at the K reactors where use of nitrogen-helium gas mixtures were being tested in place of the normal carbon dioxide-helium mixtures. Theoretical predictions of the increased C^{14} production in the gas coolant system resulting from this change in coolant gas composition have been presented by Carter(1) and Bunch(2) based on slightly different models. In both cases the C^{14} increase is related to the more favorable N^{14} (n,p) C^{14} reactions over that of C^{13} (n,γ) C^{14}. Hall, Barton and Milligan(3) considered the radiological aspect of C^{14} in reactor effluents.

As a result of an observed increase in C^{14} in K Area drier condensates several samples from reactors were analyzed, and methods for removal of C^{14} were sought. The decontamination studies showed much lower C^{14} concentrations in the condensate than anticipated. Results are reported for methods investigated for decontaminating these condensate wastes along with a general description of the wastes.

SUMMARY

Four methods for removing C^{14} containing species from condensate solutions were investigated. These methods gave the following results:

1. Acid Distillation

Distillation of volatile species from acid solution removed 20 to 80 percent of the β activity (excluding tritium) for the series of samples analyzed. Addition of potassium permanganate, ammonium persulfate or potassium periodate to the distilling system appeared to have little effect. Barium nitrate addition to the residues from the acid distillation reduced the activity to less than 10 percent of the original activity which suggests removal of S^{35} as precipitated sulfate.

2. Precipitate with Barium and Calcium Salts

Precipitation with calcium nitrate in alkaline solution removed 27 to 91 percent of the total beta activity. This step followed by barium nitrate addition increased removal to greater than 70 percent in most cases and greater than 90 percent in many cases. Precipitation with barium nitrate alone gave essentially the same effect as the coupled calcium nitrate-barium nitrate addition.

3. Ion Exchange

Equilibrium data for a strong base anion exchange resin (IRA 410) gave K_d's of 9 to 14 for K reactor condensates and 10^4 for an F area condensate.

4. Mineral Bed Reaction

The reaction: $CaSO_{4(s)} + {}^{14}CO_{3(aq)}^{=} \rightleftharpoons Ca{}^{14}CO_{3(s)} + SO_{4(aq)}^{=}$ gave K_d's from 3 to 13 for K area wastes.

Total beta activity of K area wastes (excluding tritium) based on C^{14} counting efficiency, ranged from 0.1 to 11 μc/ml. Sulfur-35 contributed 20-80 percent of the initial activity while C^{14} composed the remainder. Tritium concentrations are reported to be a factor of about 10 higher than the total other weak beta emitters present[4].

EXPERIMENTAL METHODS

Counting Technique

All samples were counted in 1-inch dishes in a gas flow counter. Twenty-five to 250 microliter aliquots were plated on dishes to which two drops of saturated barium hydroxide were added. Counting efficiency based on C^{14} standards plated as the carbonate was 14 percent. Precision of analytical results was usually within ± 20 percent, whereas the accuracy is considered to be ± 50 percent.

Acid Distillation

Initial experiments were carried out in a reaction flask connected to a train of caustic scrubbers. The solution was sparged with air passed through an Ascarite bed, and the bases and distillate evolved on boiling were collected in the scrubbing train. Samples and residue were analyzed. In these experiments the sum of the beta activity found in the scrubbers and residue agreed with the total beta activity present in the original sample. Subsequent experiments employed acid addition to covered beakers and analyses were obtained for residues only.

Precipitation Methods

Excess concentrations of calcium and barium solutions were added to samples followed by centrifugation and sampling. Carbonate concentration in the K area samples was sufficient to effect good precipitation of $^{14}CO_3^{=}$ while sulfate carrier was needed to obtain good removal of S^{35} as $Ba^{35}SO_4$.

Ion Exchange and Mineral Bed Experiments

A strong base anion exchange resin (IRA-410) was used in these experiments. The solutions and resin were equilibrated 72 hours prior to analysis of the solutions. Distribution coefficients reported express gross beta decontamination with no attempt to isolate the holdup of particular S^{35} or C^{14} species.

The mineral bed reaction:

$$CaSO_{4(s)} + {}^{14}CO^{=}_{3(aq)} = Ca^{14}CO_{3(s)} + SO^{=}_{4(aq)}$$

was investigated using 35-60 mesh gypsum particles. Mixtures of 5 gm gypsum samples and 12.5 ml of condensate waste were agitated for 72 hours prior to analyses.

RESULTS AND DISCUSSION

Acid Distillation and Precipitation

The methods investigated for removal of C^{14} from drier condensates were selected for their simplicity and on the basis of a limited knowledge of the chemical composition of these wastes. It was originally assumed that much of the C^{14} was associated with carbonate ion, and classical acid distillation and precipitation methods of carbonate removal were studied. When incomplete removal was obtained by these methods, sulfate carrier and barium solutions were added to effect removal of S^{35} existing as sulfate. The source of the activity remaining after both acid distillation and precipitation (2-30 percent) was not determined except that it was due primarily to weak beta emitters having maximum energies of < 0.2 MEV. Since iron and cyanide were found in the wastes, it is possible that stable cyanide complexes are present which could account for a portion or all of the remaining C^{14} activity. Other carbon and sulfur compounds may be present, but few would be expected to persist in boiling 2 - 4 N HNO_3 followed by precipitation with barium ion in alkaline solution. Another observation that contributes to the existence of cyanide complexes is the formation of a pinkish precipitate on addition of HCl to the wastes. This precipitate could be due to copper-iron cyanide complexes which are quite insoluble in hydrochloric acid solutions. Data for the decontamination experiments are listed in Table I. The percent of the activity removed during acid distillation from nitric acid would seem to be limited to volatile carbon compounds, those oxidizing to carbon dioxide and from cyanides. The difference in removal by acid distillation and acid distillation plus barium sulfate precipitation should then give a measure of the S^{35} concentration. Based on this criteria, an approximation of C^{14} to S^{35} ratios can be obtained. The percent activity remaining in solution after precipitation with barium gives a measure of the activity in forms other than carbonate or sulfate and amounts to 2 to 60 percent of the total. Part of this larger variation is due to analytical inaccuracies; however, trends are established. The apparent difference in the ability to decontaminate aged and current solutions is based on S^{35} decay. From these results one would predict that approximately 50 percent of the C^{14} activity was in the form of carbonate originally. The remainder of the activity in these cases may again be due in part to stable cyanide complexes.

Ion Exchange Experiments

Data for the ion exchange and mineral bed reactions are presented in Table II. The high salt concentrations of the K area wastes (about 1-3 N) would require

TABLE I

DECONTAMINATION BY ACID DISTILLATION AND PRECIPITATION

Sample Origin and Date	Percent Beta* Activity Removed			
	Acid Distillation Only	Acid Distillation + Precipitation w/Ba$(NO_3)_2$	Precipitation w/Ba$(NO_3)_2$	Precipitation w/Ca$(NO_3)_2$
KE - 8/31/61	50-65	58-66	63	58
KE - 9/ 3/61	52-67	70-76	60	67
KE -10/29/61	54-66	67-70	48	50
KW - 9/18/62	86-90	97-99	99	86-88
KE - 9/28/62	66-78	88-92	89	69-76
KE -10/24/62	16-30	94-98	90	27-55
KW -10/25/62	--	--	98	82
KE -11/12/62	37-50	88-96	80-82	72
D -11/30/62	56-60	90-93	88-90	51-53
F -11/30/62	43-49	90-98	93-97	41
KE -11/30/62	42-47	86-90	65-72	64
KW -12/ 3/62	78-80	90-93	82-84	91

*Excludes tritium

rather large quantities of resin for adequate treatment. The K_d values obtained are consistent with this since one is attempting C^{14} decontamination by removal of up to 1.0M carbonate. In the decontamination of the F Area condensate one is concerned with salts concentrations on the order of 0.01M and a correspondingly higher K_d value is obtained. A column experiment with this F Area waste reached 30 percent breakthrough after 1000 column volumes at which point the condensate sample was exhausted. The 50 percent breakthrough is estimated to be at about 1300 column volumes.

TABLE II

ION EXCHANGE AND MINERAL BED DECONTAMINATION VALUES

Conditions - Resin and Solutions Shaken for 72 Hours at Room Temperature

Sample Origin and date	Volume Waste ml	Grams Resin		$K_d = \frac{\text{Total beta / g. resin}}{\text{Total beta / ml solution}}$
KE - 9/28/62	10	3.79	IRA 410	13.0
KE - 9/28/62	10	2.96		8.8
KE - 9/28/62	20	4.82		10.0
KE - 9/28/62	20	4.89		13.3
KW - 9/18/62	20	4.62		2.7
KW - 9/18/62	20	5.12		2.6
KE - 10/24/62	20	4.25		11.1
KE - 10/24/62	20	5.00		10.8
KW - 10/25/62	20	4.45		6.2
KW - 10/25/62	20	5.24		5.2
F - 11/30/62	100	0.77		2×10^4
F - 11/30/62	100	0.77		2×10^4
KW - 9/18/62	12.5	4.91	Gypsum	3.4
KW - 9/18/62	12.5	4.67		3.1
KE - 9/28/62	12.5	5.08		10.0
KE - 9/28/62	12.5	4.45		12.0
KE - 10/24/62	12.5	5.48		10.3
KF - 10/24/62	12.5	5.12		13.6

Physical and Chemical Descriptions of Drier Condensates

Determination of chemical species present in the condensate was not included in the scope of this work as this aspect of the problem is being investigated by Barton[4]. However, a general description of the solutions is given in Table III. All K-East Area samples were dark blue in color and strongly ammoniacal, the blue color being attributed to tetramine copper (II) ion. K-West Area samples were dark blue to colorless and also strongly ammoniacal. Solutions from D and F Areas were colorless with a brownish, hydrated ferric oxide-appearing sediment present in the F Area Sample.

Values for total beta activity, excluding tritium, are also given in Table III. These data indicate approximately a ten to a hundredfold higher C^{14} concentration in the K Area condensates compared to those of D and F Areas. However, in comparing total C^{14} output (taking into account differences in volumes of condensate produced in the two cases) the difference is diminished.

CONCLUSION

Carbon-14 decontamination factors of about 2 to 10 can be obtained by the methods investigated. Further decontamination appears to require a multistep process which could best be established after determining the C^{14} containing species present in these wastes as well as their relative concentrations. In view of the low C^{14} concentrations observed as well as the low

TABLE III

DESCRIPTIONS OF DRIER CONDENSATE SAMPLES

Sample Origin and Date	Total β* μc/ml	Estimated C^{14} μc/ml	S^{35} μc/ml	pH	NH_4 moles/liter	Remarks
KE - 8/31/61	0.2	0.2	---	9.1 to 10.4	0.5 to 2	Carbonate, cyanide, copper and iron present in all K Area condensates.
KE - 9/ 3/61	0.3	0.3	---			
KE - 10/29/61	0.2	0.2	---			
KE - 9/28/62	2	1	0.1 to 7			0.8M $CO_3^{=}$ 0.03M CN^{-}
KE - 10/24/62	6	1				
KE - 11/12/62	11	4				
KE - 11/30/62	1	0.6				
KW - 9/18/62	0.1	0.06				
KW - 10/25/62	0.6	0.3				
KW - 12/ 3/62	0.6	0.5				
D - 11/30/62	0.03	0.02	0.01	5.0	0.02	0.01M $CO_3^{=}$
F - 11/30/62	0.02	0.01	0.01	7.6		

*Total β based on C^{14} counting efficiencies - tritium excluded.

total C^{14} output estimated for the drier condensate streams, attempts to obtain higher decontamination factors do not appear justified at the present time. Barton's work on characterization of the C^{14} species present in these wastes[4] and some further analyses of these wastes to obtain a good cross section of data on gross C^{14} release factors may encourage a few additional specific type decontamination experiments at a later date.

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